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<b>(54) Title:</b> CRYSTALLISABLE COPOLYESTERS  <b>(57) Abstract</b>  The present invention relates to thermoplastic copolyester compositions comprising at least 15 weight percent acid and/or glycol component modification, an inherent viscosity of greater than 0.5 dl/g, and containing at least one poly(alkylene glycol) having an alkylene chain of 2 to 10 carbon atoms. This invention also relates to procedures for incorporating the poly(alkylene glycol) into the polyester composition at any point in the polymerization. The compositions of the present invention display improved crystallization from the glass with very little change in the crystallization from the melt behavior.		

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## CRYSTALLISABLE COPOLYESTERS

## RELATED APPLICATION

- 5           This application claims the benefit of provisional application U.S. Serial No. 60/131,349 filed April 28, 1999.

## BACKGROUND

- 10           Thermoplastic polyesters are often modified by the addition of a comonomer to enhance some useful property such as gas barrier, toughness, or impact strength. Copolymer modification is also widely used to slow the rate of crystallization from the melt to enable the molding of thick amorphous parts having good optical transparency. If molded from a rapidly crystallizing homopolymer,  
15           these parts would be partially crystalline and consequently optically hazy or opaque due to the slow heat transfer characteristic of a thick part.

- Copolymer modification also slows the rate of crystallization from the glass, and this is often undesirable because it interferes with the manufacture or processing of the polymer. Some polyester homopolymers are also slow to  
20           crystallize from the glass, creating the same difficulties.

- For example, polyesters for blow molded container applications are typically manufactured in two stages: melt phase polymerization to a moderate molecular weight followed by polymerization in the solid state to further increase molecular weight. The melt phase intermediate must be pelletized and partially  
25           crystallized prior to solid state polymerization. Crystallization of the amorphous melt phase pellets is accomplished by heating them to above their glass transition temperature (crystallization from the glass) while agitating them to prevent sticking and agglomeration. It is highly desirable that the pellets crystallize rapidly; if they are slow to crystallize, agglomeration is difficult to avoid and the production rate is  
30           reduced. Furthermore, the pellets must attain a certain degree of crystallinity prior

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to introduction into the solid state polymerization reactor to avoid sticking and agglomeration in the reactor. Polyesters highly modified with a comonomer often undergo solid state polymerization at lower temperatures to avoid sticking and agglomeration in the reactor. The slow crystallization rate characteristic of polyester copolymers (and some homopolymers) may therefore slow the production rate.

The high molecular weight achieved through solid state polymerization is not required for many molding and extrusion applications. However, the pellets of most polyesters must be dried immediately prior to melt processing to minimize hydrolysis and bubble formation during processing. Crystallized pellets can be dried at a higher temperature -- and therefore more rapidly and effectively -- than amorphous pellets, so polyester pellets are often crystallized even if no subsequent solid state polymerization is done. As in the case described above, polyester copolymers and homopolymers that are slow to crystallize from the glass create manufacturing difficulties during pellet crystallization and slow the rate of production.

EP 822,213 discloses polyester compositions comprising terephthalic acid, up to 15 weight percent of a second acid component and polyalkylene glycol in amounts 0.001 to 10 percent by weight of the glycol component. The compositions are disclosed to have improved crystallization from the glass during heat setting. However, EP 822,213 does not disclose crystallizable polyesters having more than 15 weight percent acid component modification which can be fabricated into useful articles such as films or bottles.

US 3,663,653 discloses polyester compositions having up to 10 weight percent copolymer modification and 0.5 to 15 weight percent polytetrahydrofuran have good crystallization from the melt. However, crystallizable polyesters having more than 15 weight percent copolymer modification are not disclosed.

US 4,322,335 disclose polyester-polyethylene glycol block copolymers. The use of any copolyesters is not disclosed.

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As these examples illustrate, it would be highly beneficial to increase the crystallization rate from the glass of polyester compositions normally slow to crystallize, particularly while retaining a relatively slow crystallization rate from the melt, and without the substantial diminishment of desirable properties such as clarity and good color.

## DESCRIPTION OF THE INVENTION

This invention relates to new polyester compositions, processes to prepare the new polyester compositions, and articles, film, and sheet made from the new polyester compositions by molding, extrusion, or other melt processing techniques. Specifically, this invention relates to thermoplastic copolyester compositions comprising at least 15 weight percent acid component modification, an inherent viscosity of greater than 0.5 dl/g, and containing at least one poly(alkylene glycol) having an alkylene chain of 2 to 10 carbon atoms. This invention also relates to procedures for incorporating the poly(alkylene glycol) into the polyester composition at any point in the polymerization, by any one of several methods, including but not limited to (1) addition directly into the melt phase reactor, (2) addition of the poly(alkylene glycol) into the molten polyester composition after completion of melt phase polymerization but prior to strand extrusion and pelletizing, (3) compounding the poly(alkylene glycol) with polyester pellets to form a concentrate which is subsequently blended with additional polyester in the final molding or extrusion process, (4) addition of the poly(alkylene glycol) directly into the feed hopper or feed throat of the molding machine or extruder used to manufacture the final article, and (5) blending the poly(alkylene glycol) with polyester pellets prior to molding or extrusion.

We have found that a polyester copolymer modified with at least 15 weight percent, based upon the weight percent of all acid components, and preferably 15 to about 25 weight percent of a dibasic acid and about 0.01 to about 5.0 weight percent of a poly(alkylene glycol) such as poly(tetramethylene glycol) and

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poly(ethylene oxide) can be produced in a crystalline form with a high  $\text{IhV}$  of 0.5 to 1.3 dl/g. Furthermore, 0.01 to 5.0 weight percent of a poly(alkylene glycol) incorporated in a thermoplastic polyester greatly increases the crystallization rate from the glass while increasing the crystallization rate from the melt only moderately or not at all. Furthermore, modifying a polyester copolymer with about 0.01 to about 5.0 weight percent of a poly(alkylene glycol) successfully reduced or prevented the polyester pellets from sticking together during crystallization. Furthermore, modifying a polyester with about 0.01 to about 5.0 weight percent of a poly(alkylene glycol) allowed the polyester to solid state polymerized at a higher temperature and rate while successfully reducing or preventing sticking during solid state polymerization at the higher temperature. Furthermore, a polyester copolymer modified with up to 25 weight percent of a dibasic acid and 0.01 to 5.0 weight percent of a poly(alkylene glycol) such as poly(tetramethylene glycol) and poly(ethylene oxide) can be fabricated into a hollow vessel such as a bottle. The poly(alkylene glycol) does not degrade the optical properties such as clarity, transparency, and color of the polyester, both in the amorphous state and after crystallization via mechanical orientation or stretch blow molding.

The invention is particularly effective in poly(alkylene arylates) such as poly(alkylene terephthalates), poly(alkylene isophthalates), poly(alkylene naphthalates), and copolymers, blends, and mixtures thereof.

The polyester composition and process for producing the polyester are described below in detail.

Suitable polyesters comprise a glycol component and an acid component comprising a first dicarboxylic acid and at least 15 weight % of at least one second dicarboxylic acid, based upon the acid component.

The first dicarboxylic acids are terephthalic, isophthalic, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic acid, phenylenedioxidiacetic acid and the like. Preferably the first dicarboxylic acid is terephthalic acid. The various isomers of naphthalenedicarboxylic acid or mixtures of isomers may be used but the 1,4-, 1,5-, 2,6-, and 2,7-isomers are preferred. The

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1,4-cyclohexanedicarboxylic acid may be in the form of cis, trans, or cis/trans mixtures. The various isomers of phenylenedioxydiacetic acid or mixtures of isomers may be used but the 1,2-, 1,3-, 1,4- isomers are preferred. In addition to the acid forms, the lower alkyl esters or acid chlorides may be also be used.

5           The second dicarboxylic acid is present in an amount greater than 15 weight % and preferably between at least 15 to about 25 weight percent, based upon the acid component. Such additional dicarboxylic acids include dicarboxylic acids having from 6 to about 40 carbon atoms, and more preferably dicarboxylic acids selected from aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms,  
10   aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 7 to 12 carbon atoms. Examples of suitable dicarboxylic acids include phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, 1,3-  
15   phenylenedioxydiacetic acid, 1,2-phenylenedioxydiacetic acid, 1,4-phenylenedioxydiacetic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. In certain embodiments isophthalic acid is the preferred second dicarboxylic acid. Polyesters may be prepared from one or more of the above dicarboxylic acids.

20           Typical glycols used in the polyester include aliphatic glycols containing from two to about ten carbon atoms, and cycloaliphatic glycols containing 7 to 14 carbon atoms. Preferred glycols include ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol and the like. The glycol component may optionally be modified with up to about 25 weight percent, preferably up to  
25   about 20 weight percent and most preferably up to about 15 weight percent of one or more different diols. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms, aromatic diols containing from 6 to 15 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol,  
30   1,4-cyclohexanedimethanol (when using 1,4-cyclohexanedimethanol, it may be the

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cis, trans or cis/trans mixtures), propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3),

- 5 1,4-di-(2-hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 1,3-bis(2-hydroxyethoxy)benzene, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, resorcinol, hydroquinone and the like. Polyesters may be prepared from one or more of the above diols.

- 10 The poly(alkylene glycol) having an alkylene chain of 2 to 10 carbon atoms, which forms the diol constituent units, is poly(alkylene glycol) generally known. The poly(alkylene glycols) can be obtained by method well known in the art. The poly(alkylene glycol) desirably has a molecular weight of 100 to 10,000 g/mole, preferably 400 to 3000 g/mole.

- 15 Examples of poly(alkylene glycol)s include poly(ethylene glycol), poly(propylene glycol), poly(tetraethylene glycol), poly(heptamethylene glycol), poly(hexamethylene glycol) and poly(octamethylene glycol). Of these, particularly preferable is poly(tetraethylene glycol). In the present invention, it is desired that the constituent units derived from the poly(alkylene glycol) in the first polyester are  
20 contained in amounts of 0.01 to 10 percent by weight, preferably 0.01 to 8 percent by weight, more preferably 0.1 to 5 percent by weight, based on the constituent units.

- If the amounts of the constituent units derived from the poly(alkylene glycol) are less than 0.01 percent by weight, the improvement in the heat-up crystallization  
25 rate or solid state polymerization temperature of the polyester might be insufficient. If the amounts thereof exceeds 10 percent by weight, the transparency, the heat stability, the mechanical properties and the gas barrier properties of the polyester might be insufficient for some embodiments.



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Difunctional components such as hydroxybenzoic acid may also be used.

Also small amounts of multifunctional polyols such as trimethylolpropane, pentaerythritol, glycerol and the like may be used if desired.

5 The resin may also contain small amounts of trifunctional or tetrafunctional comonomers to provide controlled branching in the polymers. Such comonomers include trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, trimellitic acid, trimellitic acid, pyromellitic acid and other polyester forming polyacids or polyols generally known in the art.

10 Also, although not required, additives normally used in polyesters may be used if desired. Such additives include, but are not limited to colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, acetaldehyde reducing compounds, barrier enhancing compounds, UV absorbing compounds and the like.

15 Prior to the polycondensation of the melt-phase process, a mixture of polyester monomer (diglycol esters of dicarboxylic acids) and oligomers are produced by conventional, well-known processes. One such process is the esterification of one or more dicarboxylic acids with one or more glycols; in another process, one or more dialkyl esters of dicarboxylic acids undergo transesterification with one or more glycols in the presence of a catalyst. In either case, the monomer and  
20 oligomer mixture is typically produced continuously in a series of one or more reactors operating at elevated temperature and pressures at one atmosphere or greater. Alternately, the monomer and oligomer mixture could be produced in one or more batch reactors. Suitable conditions for esterification and transesterification include temperatures between 200 to about 250°C and pressures of about 0 to about  
25 80 psig. It should be understood that generally the lower the reaction temperature, the longer the reaction would have to be conducted.

Next, the mixture of polyester monomer and oligomers undergoes melt-phase polycondensation to produce a low molecular weight precursor polymer. The precursor is produced in a series of one or more reactors operating at elevated  
30 temperatures. To facilitate removal of excess glycols, water, alcohols, aldehydes,

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and other reaction products, the polycondensation reactors are run under a vacuum or purged with an inert gas. Inert gas is any gas not causing unwanted reaction. Suitable gases include, but are not limited to partially or fully dehumidified air, CO<sub>2</sub>, argon, helium and nitrogen. Catalysts for the polycondensation reaction include salts of antimony, germanium, tin, lead, or gallium, preferably antimony or germanium. Reactions conditions for polycondensation include a temperature less than about 290°C, and preferably between about 240°C and 290°C at a pressure sufficient to aid in removing undesirable reaction products such as ethylene glycol. Precursor IhV is generally below about 0.7 to maintain good color. The target IhV is generally selected to balance good color and minimize the amount of solid stating required. Inherent viscosity (IhV) was measured at 25°C using 0.50 grams of polymer per 100 ml of a solvent consisting of 60 percent by weight phenol and 40 percent by weight tetrachloroethane. The low molecular weight precursor polymer is typically produced continuously in a series of one or more reactors operating at elevated temperature and pressures less than one atmosphere. Alternately low molecular weight precursor polymer could be produced in one or more batch reactors.

After pelletization of the low molecular weight precursor polymer, the pellets may be fed directly into an extruder, or solid stated at conventional conditions until the desired molecular weight is attained.

Another key feature of the invention is that the precursor is crystallized and undergoes further polycondensation in the solid state by conventional, well-known processes, such as those disclosed in U.S. Pat. No. 4,064,112. Solid state polycondensation can be conducted in the presence of an inert gas as defined above, or under vacuum conditions, and in a batch or continuous process. The polyester can be in the form of pellets, granules, chips or powder. Temperature during the solid state polycondensation process should be about 1 to 60°C below the melting point of the polyester as measured by differential scanning calorimetry (DSC). What is significant and unexpected with respect to the present invention is that the low molecular weight precursor polymer containing low levels of

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poly(alkylene glycol)s can be solid state polymerized at temperatures nearer to its melting point without sticking or agglomeration. Polyesters containing poly(alkylene glycol)s can be solid state polymerized at a rate higher than the same polyester without the poly(alkylene glycol). Thus polyesters containing

5 poly(alkylene glycol)s can be produced more efficiently.

Polyesters displaying selectively improved crystallization from the glass may be produced by any one of several methods. The poly(alkylene glycol) may be added at nearly any point in the polyester manufacturing process or during article fabrication. Some of the most beneficial aspects of the improved

10 crystallization are seen during crystallization prior to solid stating and during solid stating. Thus, for improvement in pellet crystallization, addition is preferably made prior to pelletizing the low molecular weight precursor polymer.

The poly(alkylene glycol) may be added directly into the melt phase reactor during esterification, prepolymer or polycondensation stages. If this method is

15 used it is desirable to add the poly(alkylene glycol) at a point in the reactors where there is good mixing to insure homogeneous distribution of the poly(alkylene glycol) throughout the polymer melt. The poly(alkylene glycol) may be added undiluted directly to the polymer melt or incorporated into a liquid carrier and added to the polymer melt. If a liquid carrier is used the poly(alkylene glycol) may

20 incorporated into the liquid carrier at concentrations of 1 to 99 weight percent. The liquid carrier may be any organic solvent or water. Preferably, the liquid carrier is ethylene glycol.

In an alternate embodiment the poly(alkylene glycol) may be undiluted or incorporated into a low molecular weight, polymeric or liquid carrier and added to

25 the molten polyester composition after completion of polycondensation but prior to strand extrusion and pelletizing.

Alternatively, in some embodiments the desired amount of the poly(alkylene glycol) or a poly(alkylene glycol) concentrate may be fed directly with the polyester pellets into the feed hopper or feed throat of the molding machine or

30 extruder used to manufacture the final article.

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The poly(alkylene glycol) may also be incorporated in a liquid carrier and introduced into an extruder. Suitable liquid carrier systems include those made by Colormatrix, Inc. Addition of the poly(alkylene glycol) after pelletization is particularly useful for making shaped articles, such as containers, which require thermal treatments after being formed.

Stretch blow molded containers made from the polyester of the present invention may be produced by either the one step extrusion blow molding method or the two step reheat blow mold method. The stretching temperature is 70° to 120° C, preferably 80° to 110° C, and the stretching ratio is 1.5 to 3.5 times in the machine direction and 2 to 5 times in the hoop direction.

If desired, the stretched bottles may be used as is or heatset in a mold at a temperature of not lower than 100°C. The finish of the preform of the heatset bottles may be thermally crystallized before stretch blow molding or the finish may be thermally crystallized after stretch blow molding.

The polyester of the present invention may make up one or more layers of a multilayer that includes one or more barrier layers such as a polyamide, EVOH or a layer containing an oxygen scavenger.

It is also possible to form a uniaxially or biaxially stretched film from a polyester of the present invention or a can-shaped container, a tray or the like by vacuum forming or air-pressure forming after it is formed into a sheet by injection molding. It is also possible to form a polyester of the present invention into a multi-layered sheet of the polyester and polyethylene terephthalate, for example, by a multi-layer extruder and thereafter form the sheet into a uniaxially or biaxially stretched film, a can-shaped container or a tray.

A polyester composition of the present invention can be formed into a film, sheet, container, and other packaging material by a melt molding method which is generally used in molding polyethylene terephthalate. The polyester composition is usable as a material having a high gas barrier property in an unstretched state. By stretching the polyester composition at least uniaxially, it is possible to improve the gas barrier property and the mechanical strength.

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A stretched sheet of a polyester composition of the present invention is produced by stretching a polyester of the present invention which has been formed into a sheet by injection molding or extrusion molding. The stretching method adopted may be freely selected from uniaxially stretching, sequential biaxially stretching and simultaneous biaxially stretching. It is also possible to form a stretched sheet of a polyester composition of the present invention into a cup or a tray by air-pressure forming.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

The inherent viscosity,  $\eta_{\text{inh}}$ , was measured at 25°C at a concentration of 0.5 g/dL in a 60/40 weight percent mixture of phenol/tetrachloroethane.

The crystallization behavior of the films was characterized using a differential scanning calorimeter (DSC).

First, the isothermal crystallization half-time was measured by heating rapidly from the glassy state (after an initial heat/quench to destroy any pre-existing crystallinity) to either 140, 150 or 160°C and then maintaining that temperature, and also by cooling rapidly from the molten state to either 140, 160, or 180°C and then maintaining that temperature. The shorter the crystallization half-time, the faster the rate of crystallization.

The film was heated in the DSC to 290°C to destroy any pre-existing crystallinity, then quenched to room temperature to create a glassy amorphous sample, then heated at a rate of 20°C/min. The crystallization temperature on heating,  $T_{\text{ch}}$ , was determined from the peak of the exothermic transition. The crystallization temperature from the melt ( $T_{\text{cc}}$ ) was determined from the peak of the exothermic transition observed while cooling the sample from 290°C at 20°C per minute.

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**Example 1 – PET copolymer modified with 15.0 weight percent dimethyl isophthalate**

Dimethyl terephthalate (0.425 mol, 82.45 g), dimethyl isophthalate (0.075 mol., 14.55 g), ethylene glycol (1.0 mol, 62 g), manganese acetate ( 0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had an IhV of 0.65 dL/g. Thermal analysis results are listed in Table 1. The ground polymer was crystallized at 150°C for two hours. The ground polymer was sifted over a 850 micron sieve. The polymer (12 grams) was then placed in a solid state unit having a nitrogen purge and heated at 197°C. The ground polymer was stuck together after 9 hours in the solid state unit.

**Example 2 – PET copolymer modified with 15.0 weight percent dimethyl isophthalate**

**and 0.5 wt. percent PTMG**

Dimethyl terephthalate (0.425 mol, 82.45 g), dimethyl isophthalate (0.075 mol., 14.55 g), poly(tetramethylene glycol) ( $M_n = 1000$  g/mole, 0.48 mmol, 0.48 g), ethylene glycol (1.0 mol, 62 g), manganese acetate ( 0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had

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an IhV of 0.63 dL/g. Thermal analysis results are listed in Table 1. The ground polymer was crystallized at 150°C for two hours. The ground polymer was sifted over a 850 micron sieve. The polymer (12 grams) was then placed in a solid state unit having a nitrogen purge and heated at 197°C. The ground polymer did not stick together after 21 hours in the solid state unit.

**Example 3 – PET copolymer modified with 15.0 weight percent dimethyl isophthalate and 1.0 wt. percent PTMG**

Dimethyl terephthalate (0.425 mol, 82.45 g), dimethyl isophthalate (0.075 mol., 14.55 g), poly(tetramethylene glycol) ( $\langle M_n \rangle = 1000$  g/mole, 0.97 mmol, 0.97 g), ethylene glycol (1.0 mol, 62 g), manganese acetate (0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had an IhV of 0.63 dL/g. Thermal analysis results are listed in Table 1. The ground polymer was crystallized at 150°C for two hours. The ground polymer was sifted over a 850 micron sieve. The polymer (12 grams) was then placed in a solid state unit having a nitrogen purge and heated at 197°C. The ground polymer did not stick together after 21 hours in the solid state unit.

**Table 1: PET modified with 15 weight percent dimethyl isophthalate and PTMG**

Example #	PTMG (wt. %)	T <sub>ch</sub> (°C)	T <sub>cc</sub> (°C)	DSC Crystallization Half-time (min) from glass at		
				140°C	150°C	160°C
1	0	179	n.d.	13.4	9.8	7.7
2	0.5	171	n.d.	3.4	2.7	2.6
3	1.0	158	n.d.	2.0	1.5	1.4

n.d. – none detected

Thus in the above Table, the addition of PTMG reduces crystallization half time from the glass by as much as 81% at 160°C. Similarly, crystallization temperatures from the glass (T<sub>ch</sub>) also decreased as PTMG was added. From a processing standpoint, the decrease in T<sub>ch</sub> provides greatly improved solid stating, because the surface of the pellets crystallizes readily and remains non-tacky, thus, preventing sticking. There is nothing in the prior art suggesting that PTMG could improve the crystallization of a highly modified copolymer to an extent sufficient to improve solid stating. Beneficially, there was no significant change in crystallization from the melt (T<sub>cc</sub>). This is particularly important for forming articles via injection molding (such as preforms) because the injection molding processing window is not affected.

**Example 4 – PET copolymer modified with 18.0 weight percent dimethyl isophthalate**

Dimethyl terephthalate (0.41 mol, 79.45 g), dimethyl isophthalate (0.09 mol, 17.46 g), ethylene glycol (1.0 mol, 62 g), manganese acetate ( 0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and



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maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had an IhV of 0.55 dL/g. Thermal analysis results are listed in Table 2.

**Example 5 – PET copolymer modified with 18.0 weight percent dimethyl isophthalate and 0.5 weight percent PTMG**

Dimethyl terephthalate (0.41 mol, 79.45 g), dimethyl isophthalate (0.09 mol., 17.46 g), poly(tetramethylene glycol) ( $\langle M_n \rangle = 1000$  g/mole, 0.48 mmol, 0.48 g), ethylene glycol (1.0 mol, 62 g), manganese acetate (0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had an IhV of 0.62 dL/g. Thermal analysis results are listed in Table 2.

**Example 6 – PET copolymer modified with 18.0 weight percent dimethyl isophthalate and 1.5 weight percent PTMG**

Dimethyl terephthalate (0.41 mol, 79.45 g), dimethyl isophthalate (0.09 mol., 17.46 g), poly(tetramethylene glycol) ( $\langle M_n \rangle = 1000$  g/mole, 1.46 mmol, 1.46 g), ethylene glycol (1.0 mol, 62 g), manganese acetate (0.095 mmol, 0.017 g) and antimony(III)oxide (0.086 mmol, 0.025 g) were placed in a 0.5 L polymerization reactor under a nitrogen atmosphere. The mixture was heated with stirring at 200°C for 90 min. The temperature was increased to 220°C and maintained for 70 min. Phosphoric acid (0.28 mmol, 0.027 g) was added to the mixture. The temperature was increased to 280°C, the nitrogen flow was stopped and vacuum

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applied. The polymer was stirred under vacuum (0.2 mm Hg) for 90 min. The polymer was cooled and ground to pass through a 3 mm screen. The polymer had an lhV of 0.62 dL/g. Thermal analysis results are listed in Table 2.

5      **Table 2: PET modified with 18 weight percent dimethyl isophthalate and PTMG**

Example #	PTMG (wt. %)	T <sub>ch</sub> (°C)	DSC Crystallization Half-time (min) from glass at		
			140°C	150°C	160°C
4	0	n.d.	17.8	12.3	12.4
5	0.5	177	5.4	4.2	4.9
6	1.5	171	4.1	3.1	3.3

n.d. – none detected

10      The data in Table 2 shows that crystallization from the glass is improved for copolymer modifications greater than 15 weight percent. Below 15 weight percent modification, the copolymers can be crystallized in a reasonable time using commercial processes. For example, we measured the crystallization halftime of PET modified with 12 weight percent dimethyl isophthalate to be 4.2 seconds at 160°C from the glass without any crystallization aids. Thus, PET modified with 12 weight percent dimethyl isophthalate crystallizes much faster than Example 4 (18 weight % modification). Copolyesters containing greater than 15 weight percent of a comonomer are undesirably slow to crystallize. It is thus surprising that incorporating PTMG into the copolyesters containing greater than 15 weight percent (Examples 5 and 6) decreases the crystallization halftime to amount similar to PET modified with 12 weight percent dimethyl isophthalate. These copolyesters with modifications greater than 15 weight percent and containing PTMG can be crystallized in a reasonable time

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In the specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

## CLAIMS

1. A polyester comprising a dicarboxylic acid component comprising terephthalic acid and glycol component comprising ethylene glycol wherein said polyester further comprises at least 15 weight percent of a second dicarboxylic acid or second glycol component or mixture thereof; and about 0.01 to about 5 weight percent of at least one poly(alkylene glycol), wherein said polyester displays selectively improved crystallization from the glass compared to a polyester without said at least one poly(alkylene glycol).
2. The composition of claim 1 wherein said polyester comprises between at least 15 and about 25 weight percent of a second dicarboxylic acid or glycol component or mixture thereof
3. The polyester of claim 1 wherein said dicarboxylic acid component comprises at least 15 weight percent of at least one second dicarboxylic acid.
4. The polyester of claim 1 wherein said second acid component is selected from the group consisting of isophthalic acid, naphthalene dicarboxylic acid, 1,2-phenylenedioxydiacetic acid, 1,3-phenylenedioxydiacetic acid, 1,4-phenylenedioxydiacetic acid, cyclohexane diacetic acid, adipic acid and mixtures thereof.
5. The polyester of claim 1 wherein said second acid component comprises isophthalic acid.
6. The polyester of claim 1 wherein said second glycol component is selected from the group consisting of cyclohexane dimethanol, propane-1,3-diol, butane-1,4-diol, neopentyl glycol, diethylene glycol and mixtures thereof.
7. The polyester of claim 1 wherein said poly(alkylene glycol) comprises an alkylene chain of 2 to 10 carbon atoms.
8. The polyester of claim 1 wherein said poly(alkylene glycol) is selected from the group consisting of poly(ethylene glycol), poly(propylene glycol), poly(tetraemethylene glycol), poly(heptamethylene glycol), poly(hexamethylene glycol), poly(octamethylene glycol) and mixtures thereof.

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9. The polyester of claim 1 wherein said poly(alkylene glycol) comprises poly(tetramethylene glycol).

10. The polyester of claim 1 wherein said poly(alkylene glycol) is present in an amount between about 0.01 and about 2 weight percent.

5 11. The polyester of claim 1 wherein said polyester comprises a crystallization halftime from the glass at 140°C of less than about 5 seconds.

12. A process comprising providing a polyester comprising a first dicarboxylic acid component, a first glycol component and at least about 10 weight percent of at least one second dicarboxylic acid or second glycol component or  
10 mixture thereof; and about 0.01 to about 5 weight percent of at least one poly(alkylene glycol); and crystallizing said polyester at conditions (temperature, time or combination) thereof which is at least about 10 percent less than the conditions for a polyester which is substantially free from poly(alkylene) glycol.

13. The process of claim 12 further comprising the step of solid stating said  
15 polyester.

14. The process of claim 13 wherein said solid stating conditions are up to about 5 percent shorter than those for a polyester which is substantially free from poly(alkylene) glycol.

15. The process of claim 12 wherein said polyester further comprises at  
20 least about 15 weight percent of a second dicarboxylic acid or glycol component or mixture thereof

16. The process of claim 12 wherein said dicarboxylic acid component comprises at least 15 weight percent of at least one second acid component.

17. The process of claim 12 wherein said second acid component is  
25 selected from the group consisting of isophthalic acid, naphthalene dicarboxylic acid, 1,2-phenylenedioxydiacetic acid, 1,3-phenylenedioxydiacetic acid, 1,4-phenylenedioxydiacetic acid, cyclohexane diacetic acid, adipic acid and mixtures thereof.

18. The process of claim 12 wherein said second dicarboxylic acid  
30 component comprises isophthalic acid.

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19. The process of claim 12 wherein said poly(alkylene glycol) comprises an alkylene chain of 2 to 10 carbon atoms.

20. The process of claim 12 wherein said poly(alkylene glycol) is selected from the group consisting of poly(ethylene glycol), poly(propylene glycol),  
5 poly(tetraethylene glycol), poly(heptamethylene glycol), poly(hexamethylene glycol), poly(octamethylene glycol) and mixtures thereof.

21. The process of claim 12 wherein said poly(alkylene glycol) comprises poly(tetraethylene glycol).

# INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 00/11009

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G63/672

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 822 213 A (MITSUI PETROCHEMICAL IND) 4 February 1998 (1998-02-04) page 4, line 7 - line 14 page 5, line 11 page 5, line 21 - line 23 page 5, line 35 page 5, line 38 - line 41 page 11, line 42 - line 43 examples 4,7	1-21
A	DATABASE WPI Week 198203 Derwent Publications Ltd., London, GB; AN 1982-05022e XP002144638 & JP 56 159220 A (MITSUBISHI CHEM IND LTD) abstract	1-5,7-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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